

Energy-scanned Photoelectron Diffraction Study of Pd{110}-(2x1)p2mg-CO

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Saturation coverage (1.0 ML) of CO on many common fcc (110) surfaces leads to a (2x1)-glide plane LEED pattern. In all cases the CO molecules are believed to be located along the top of the ridges with adjacent molecules tilted in alternate directions away from the close-packed direction to minimise steric repulsion; it is this tilting which gives rise to the glide plane symmetry. The adsorption site of the CO on the ridges is dependent on the nature of the substrate. For example, on Pt{110} the CO molecules occupy atop sites while on Ni{110} the CO occupies 2-fold bridge sites. The adsorption site of CO in the (2x1)p2mg overlayer on Pd{110} has been the subject of some controversy. A quantitative LEED study found that the CO occupied the atop site [1]. This result was in disagreement with the accepted interpretation of vibrational data - the 2003 cm⁻¹ frequency of the C-O stretch had been taken to indicate a 2-fold bridge site [2]. Later work, including XPD [3] and theoretical calculations [4,5], strongly favoured the 2-fold short bridge site. An independent, fully quantitative investigation of the CO adsorption site has therefore been undertaken using the technique of energy-scanned photoelectron diffraction (PhD).

In PhD the intensity of an adsorbate core level photoemission peak is measured as a function of kinetic energy in the range 50-500 eV in a number of different emission directions. The kinetic energy dependence of the photoemission intensity results from coherent interference between the directly emitted component of the photoelectron wavefield and other components which have been elastically scattered at neighbouring atoms. Comparison of the experimental intensity-kinetic energy modulations with the results of multiple-scattering simulations allows the local structural environment of the emitter atom to be determined quantitatively.

In order to use PhD to study adsorbates on substrates such as Pd which have strong Auger features in the kinetic energy region scanned, it is essential to use high resolution, high flux synchrotron radiation sources such as the ALS. The high resolution is needed to effectively separate the adsorbate photoemission peak from the broader (fixed kinetic-energy) Auger peaks which pass through the background. All the PhD data in the current study were taken at the UltraESCA endstation of beamline 7.0.1. The Pd{110} crystal was cleaned by Ar sputtering and annealing to 720°C followed by exposure to 1x10⁻⁷ mbar of O₂ at 550°C for 5 minutes to remove residual carbon. The surface order and cleanliness were checked with LEED and soft X-ray (synchrotron radiation) photoelectron spectroscopy respectively. The crystal was cooled to -140°C and 4 L of CO was dosed to give saturation coverage and the required (2x1)p2mg LEED pattern. Even at the high resolution of this beamline the O 1s peak could not be resolved from the Pd 3p_{3/2} peak, so only C 1s PhD spectra were recorded. A total of thirteen C 1s PhD spectra were obtained covering a wide range of polar angles in the four principal azimuths of the surface. Each PhD spectrum consisted of 150 electron distribution curves (EDCs) centred about the C 1s photoemission peak. For each successive EDC the wavevector of the incident light was incremented by 0.044 from a starting value of 4.74 to an end value of 10.9. This gave a kinetic energy range of 85 to 450 eV for each PhD spectrum.

The individual EDCs of each PhD spectrum were integrated using a simple step-Gaussian function to fit the data. The high resolution provided by the ALS enabled the C 1s photoemission peak to be resolved and integrated as it passed over the broad Pd MNN Auger features at 240, 270 and 330 eV. The resulting peak intensity versus kinetic energy curve was normalised using a spline function to model the non-diffractive intensity and this gave the final modulation function. A representative selection of the modulation functions is shown in Fig. 1.

The data are currently being analysed by comparing the experimental modulation functions with the results of spherical-wave multiple-scattering calculations for different model adsorption geometries. It is planned to test all possible positions of the CO along the close-packed rows, not just the high symmetry atop and 2-fold bridge sites, to ensure that the true structure is found.

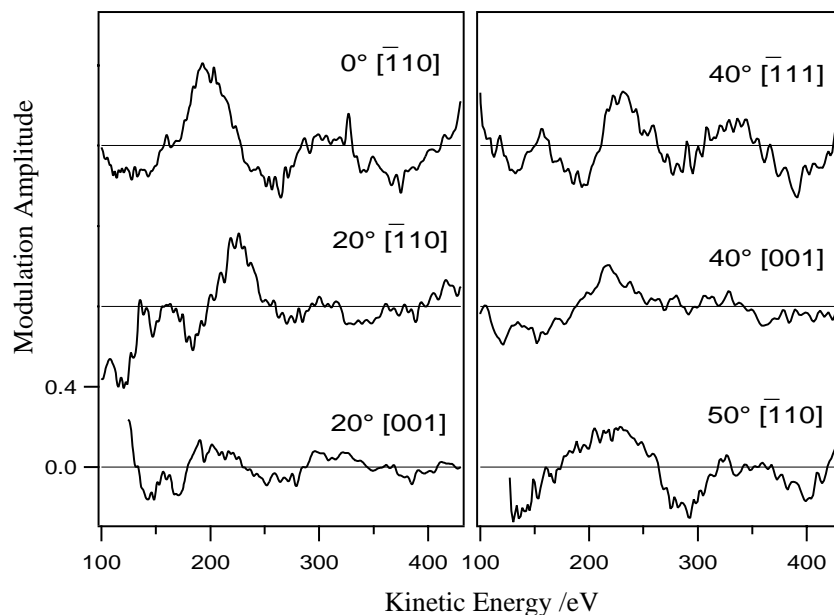


Figure 1. Modulation functions for C 1s photoemission from the (2x1)p2mg overlayer of CO on Pd{110}.

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